## PATENT ABSTRACTS OF JAPAN

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# (54) THERMALLY SHRINKABLE POLYESTER-BASED FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a thermally shrinkable polyester-based film which has a good shrunk finish property, even when used for full labels, and has a function capable of reinforcing a shrunk-covered container, an anti-blocking property, an excellent film-producing property, and excellent processability, and to provide a thermally shrinkable label using the film.

SOLUTION: This thermally shrinkable polyester-based film is characterized by having (A) a thermal shrinkage rate of 10 to 50 % in the maximum shrinkage direction in 70° C hot water, (B) a thermal shrinkage rate of ≥75 % in the maximum shrinkage direction and a shrinkage rate of ≤10 % in the direction orthogonal to the maximum shrinkage direction in 85° C hot water, (C) a thermal shrinkage rate difference  $\Delta$  (%) of 10 to 20 %, wherein  $\Delta$  is represented by expression: Δ=X0-X10; X0 (%) is a thermal shrinkage rate in the maximum shrinkage direction in 95° C hot water; X10 (%) is a thermal shrinkage rate of the 10 % thermally shrunk film in 95° C hot water, (D) a three-dimensional surface roughness S∆a of 0.008 to 0.04: and (E) a three-dimensional surface roughness SRz of 0.6 to 1.5  $\mu$  m.

[Claim(s)]

[Claim 1]

A heat contraction nature polyester system film being a heat contraction nature polyester system film, and being what satisfies following (A) - (E).

- (A) A heat shrinkage rate of a maximum shrinkage direction when it was immersed for 5 seconds into 70 \*\* warm water, and it pulled up about a sample of a heat contraction nature polyester system film cut off 10 cm x 10 cm in the shape of a square, and it is immersed for 10 seconds subsequently to underwater [25 \*\*] and pulls up is 10 to 50%.
- (B) About a sample of a heat contraction nature polyester system film cut off 10 cm x 10 cm in the shape of a square. A heat shrinkage rate of a direction to which a maximum shrinkage direction and a heat shrinkage rate of a maximum shrinkage direction when it was immersed for 5 seconds into 85 \*\* warm water, and it pulled up, and it is immersed for 10 seconds subsequently to underwater [25 \*\*] and pulls up cross at right angles not less than 75% is 10% or less.
- (C) A sample of a heat contraction nature polyester system film cut off  $10~\rm cm \times 10~\rm cm$  in the shape of a square, And about a sample which cut off a film made [ a maximum shrinkage direction ] to carry out heat contraction 10%  $10~\rm cm \times 10~\rm cm$  in the shape of a square. The heat shrinkage rate difference delta (%) shown by a lower formula when making into  $X_0$  (%) and  $X_{10}$  (%) a heat shrinkage rate of a maximum shrinkage direction measured when it was immersed for 5 seconds into 95 \*\* warm water, and it pulled up, and it is immersed for 10 seconds subsequently to underwater [  $25~\rm **$  ] and pulls up, respectively is 10 to 20%. delta =  $X_{-}X_{-}X_{-}$
- (D) The three-dimensional surface roughness Sdeltaa is 0.008-0.04.
- (E) The three-dimensional surface roughness SRz is 0.6-1.5 micrometers.

[Claim 2]

The heat contraction nature polyester system film according to claim 1 which is what is carried out about a lubricant particle whose mean particle diameter is 0.01-4 micrometers as for 0.02-0.5 mass % content.

[Claim 3]

When a thermal-shrinkage-stress value about this direction of a film after carrying out heat contraction to a maximum shrinkage direction 10% is measured on with specimen 20 mm in width, and a distance between zippers of 100 mm conditions among a 5 m [ in temperature of 90 \*\*, and blow-off speed ]/second hot wind, The heat contraction nature polyester system film according to claim 1 or 2 whose maximum-heat-shrinkage-stress value is 7 or more MPa.

[Claim 4]

The heat contraction nature polyester system film according to any one of claims 1 to 3 whose thickness distribution which specifies thickness displacement measurement in a maximum shrinkage direction of a film below when a specimen 50 cm in length and 5 cm in width is followed is 6% or less.

Thickness distribution = [(the maximum thickness-minimum thickness) /average thickness]  $\times 100$ 

[Claim 5]

The heat contraction nature polyester system film according to any one of claims 1 to 4 whose melt resistivity value in 275 \*\* is below 0.70x10<sup>8</sup> omega-cm.

[Claim 6]

A heat contraction nature label using the heat contraction nature polyester system film according to any one of claims 1 to 5.

#### DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Field of the Invention]

[0001]

This invention relates to the heat contraction nature label using the suitable heat contraction nature polyester system film for a label use, and this film.

[Background of the Invention]

[0002]

The heat contraction nature plastic film is widely used for the use of a shrink package, a shrink label, etc. using the character contracted with heating. Oriented films especially, such as a polyvinyl chloride system film, a polystyrene system film, and a polyester system film, In various containers, such as a polyethylene terephthalate (PET) container, a polyethylene container, and glassware, it is used for the purpose of a label, a cap seal, or an accumulation package (for example, patent documents 1).

[0003]

However, the polyvinyl chloride system film has problems, like heat resistance is low, generates hydrogen chloride gas at the time of incineration, or causes dioxin. If a heat contraction nature VCM/PVC system resin film is used as shrink labels, such as a PET container, when carrying out recycling use of the container, there is a problem that a label and a container must be separated.

[0004]

On the other hand, although the point whose result appearance nature after contraction of a polystyrene system film is good can be evaluated, since it is inferior to solvent resistance, the ink of a special presentation must be used in the case of printing. It is necessary to incinerate polystyrene system resin at an elevated temperature and also and it has the problem that a lot of black smokes and nasty smells at the time of incineration occur. [0005]

The polyester system film without these problems is dramatically expected as a shrink label which replaces a polyvinyl chloride system film and a polystyrene system film.

The amount used is also increasing with the amount-used increase of a PET container.

#### [0006]

With the gestalt of this film roll, after manufacture, these heat contraction nature films are once rolled round by rolled form, are sent to the presswork of various patterns, and after the end of printing. If needed, slit processing is carried out according to the size of the label etc. which are used for a final product, and the right-and-left-ends part of a film is further piled up by solvent bonding or other means, a seal is carried out, it is made a tube shape object, the thing of this tube shape object is judged, and it is processed into the gestalt of a label, a bag, etc. And the contraction tunnel (steam tunnel) of the type which equips a container with a label or a saccate thing and to which heat contraction of the steam is sprayed and carried out, A hot wind is sprayed, the inside of the contraction tunnel (hot wind tunnel) of the type which carries out heat contraction is put on a band conveyor etc., and is passed, heat contraction is carried out, and it is made to stick to a container.

By the way, from a viewpoint of recycling, use of a colored PET bottle follows on being restricted, it replaces with coloring of the bottle itself, and the demand (what is called a full label use) of a wrap is also growing with the label made from a heat contraction nature polyester system film in the great portion of bottle side. However, the side shape of a PET bottle is various, and since an outer diameter changes in arbitrary height positions, the grades of contraction that at least one label which covers the bottle whose number is one is required differ in the height position of a bottle. For this reason, even when it has conventionally better shrink characteristics than elegance and is used for covering of the bottle of complicated side shape, the heat contraction nature polyester system film which can demonstrate the outstanding contraction result nature is called for.

For example, with the PET bottle of the bevel use, the case where label wearing and contraction are performed all over a drink charging line is increasing for the productivity drive. Since such a charging line is a high speed, wearing and contraction of a label also become high-speed, and is in the tendency for contraction to be performed for a short time. Therefore, the heat contraction nature polyester system film is asked also for the physical properties which can be equal to high-speed wearing, and the contraction performance which serves as high contraction for a short time.

[0009]

In addition, these days, the operation which reinforces these containers is also being expected from the label used for various containers, such as a PET bottle. However, the label obtained from the conventional heat contraction nature polyester system film cannot satisfy such a reinforcing operation.

[0010]

In the label, although the container which carried out covering contraction packed up in the hot state in many cases (packing etc.), when it was especially a full label, the problem of pasting up mutually (blocking) also had a label between the packed-up containers.

[0011]

In addition, for a heat contraction nature film to make it run a long film at high speed, or to roll it round at high speed and to use it as a film roll from a viewpoint of a productivity drive, in a film production process or a post-processing process, is desired.

It is called for that slide nature is good to some extent so that it can respond to this.

When the slide nature of a film is insufficient, poor handling occurs at the time of a run at a high speed, or rolling up. A film specifically in the part in contact with a guide roll at the time of a film run, for example. Tension increases, an abrasion may occur in a film surface or the fault (minute projection formed without the exhaust air bit between films having fallen out) of wrinkles or the shape of a pimple may occur on the film rolled round by the roll.

[Patent documents 1] JP,H7-138388,A (paragraph numbers 0001-0005)

[Description of the Invention]

[Problem(s) to be Solved by the Invention]

Γ0012<sub>1</sub>

This invention is made in light of the above-mentioned circumstances, and the purpose, Even if it uses for a full label, good contraction result nature can be demonstrated, and it has the function and the good blocking resistance which can reinforce the container which carried out contraction covering, and is in providing the heat contraction nature label using the heat contraction nature polyester system film which was further excellent in film production nature and processability, and this film.

[Means for Solving the Problem]

[0013]

A heat contraction nature polyester system film of this invention which could attain the above-mentioned purpose has a gist at a place which is what satisfies following (A) - (E).

- (A) A heat shrinkage rate of a maximum shrinkage direction when it was immersed for 5 seconds into 70 \*\* warm water, and it pulled up about a sample of a heat contraction nature polyester system film cut off 10 cm x 10 cm in the shape of a square, and it is immersed for 10 seconds subsequently to underwater [25 \*\*] and pulls up is 10 to 50%.
- (B) About a sample of a heat contraction nature polyester system film cut off 10 cm x 10

cm in the shape of a square. A heat shrinkage rate of a direction to which a maximum shrinkage direction and a heat shrinkage rate of a maximum shrinkage direction when it was immersed for 5 seconds into 85 \*\* warm water, and it pulled up, and it is immersed for 10 seconds subsequently to underwater [ 25 \*\* ] and pulls up cross at right angles not less than 75% is 10% or less.

- (C) A sample of a heat contraction nature polyester system film cut off 10 cm x 10 cm in the shape of a square, And about a sample which cut off a film made [ a maximum shrinkage direction ] to carry out heat contraction 10% 10 cm x 10 cm in the shape of a square. The heat shrinkage rate difference delta (%) shown by a lower formula (1) when making into X<sub>0</sub> (%) and X<sub>10</sub> (%) a heat shrinkage rate of a maximum shrinkage direction measured when it was immersed for 5 seconds into 95 \*\* warm water, and it pulled up, and it is immersed for 10 seconds subsequently to underwater [ 25 \*\* ] and pulls up. respectively is 10 to 20%.  $delta = X_0 - X_{10}$  (1).
- (D) The three-dimensional surface roughness Sdeltaa is 0.008-0.04.
- (E) The three-dimensional surface roughness SRz is 0.6-1.5 micrometers.

[0014]

As for the above-mentioned heat contraction nature polyester system film, it is preferred that 0.02-0.5 mass % content is what is carried out about a lubricant particle whose mean particle diameter is 0.01-4 micrometers.

[0015]

The above-mentioned heat contraction nature polyester system film, When a thermal-shrinkage-stress value about this direction of this film after carrying out heat contraction to a maximum shrinkage direction 10% is measured on with specimen 20 mm in width, and a distance between zippers of 100 mm conditions among a 5 m [ in temperature of 90 \*\*, and blow-off speed ]/second hot wind, it is preferred that a

maximum-heat-shrinkage-stress value is 7 or more MPa.

[0016]

It is recommended that thickness distribution as which the above-mentioned heat contraction nature polyester system film specifies thickness displacement measurement in a maximum shrinkage direction of this film at a lower ceremony (2) when a specimen 50 cm in length and 5 cm in width is followed is 6% or less.

Thickness distribution = [(the maximum thickness-minimum thickness) /average thickness] x100 (2).

[0017]

In addition, as for the above-mentioned heat contraction nature polyester system film, it is preferred that a melt resistivity value in 275 \*\* is below 0.70x108 omega-cm.

[0018]

A heat contraction nature label using the above-mentioned heat contraction nature

polyester system film is also included by this invention.

[Effect of the Invention]

[0019]

Even if the heat contraction nature polyester system film of this invention is a case where high contraction is required selectively, it can acquire beautiful contraction result appearance by contraction in a low temperature region comparatively. Film production nature and processability are good. The heat contraction nature label obtained from the heat contraction nature polyester system film of this invention is excellent in the reinforcing effect of a covering container, and the above—mentioned blocking resistance. [0020]

Therefore, the heat contraction nature polyester system film and heat contraction nature label of this invention are suitable for various covering labels including full labels, such as a PET bottle, etc.

[Best Mode of Carrying Out the Invention]

[0021]

The heat contraction nature polyester system film of this invention is obtained using the mixture of the single copolymerized polyester which uses as a main component unit the ester unit formed from a publicly known polyvalent carboxylic acid component and a polyhydric alcohol component, or two or more polyester.

[0022]

The heat contraction nature polyester system film of this invention is 10% or less towards the maximum shrinkage direction and heat shrinkage rate measured on condition of the above (A) and (B) crossing at right angles not less than 75% in less than more than (A):10%50% and (B):maximum shrinkage direction. With such a film, the heat contraction nature label which serves as high contraction by short~time processing comparatively can be provided.

[0023]

Usually, at the process which carries out covering contraction to a container etc., the label made from a heat contraction nature film. In an above-mentioned hot wind tunnel, the inside of the hot wind of about 120-200 \*\* and about 2-20 m/second of wind speeds is passed in about 2 to 20 seconds, and it carries out by passing the inside of about 75-95 \*\* and the steam of about 0.5-20 MPa of pressures in about 2 to 20 seconds in a steam tunnel. (A) And the film with which all the heat shrinkage rates of (B) are satisfied of a mentioned range, For example, containers, such as a PET bottle which has complicated side shape, are received, Use this the greater part of side as a heat contraction nature label of a wrap sake, or, Even if it uses it as a heat contraction nature label for containers which has the side shape which requires partial very high contraction of a wrap label for the side (even if it uses it for for example, the full label for PET bottles, the full label for glass bottles, etc.), Very beautiful

contraction result appearance can be attained under such contraction conditions usually performed.

[0024]

That is, when the heat shrinkage rate measured on condition of (A) is less than a mentioned range, low-temperature shrinkage characteristics will need to become insufficient, and it will be necessary to make high temperature at the time of label covering contraction, and is not desirable. On the other hand, when the heat shrinkage rate measured on condition of (A) exceeds a mentioned range, it is in the tendency which defects, such as a jump (shift up when a film contracts rapidly) of the label by heat contraction, produce. As for the heat shrinkage rate measured on condition of (A), it is preferred that it is [ not less than 15% ] 40% or less.

[0025]

When the heat shrinkage rate of the maximum shrinkage direction measured on condition of (B) is less than a mentioned range, when a PET bottle etc. are made to carry out covering contraction as a label, it is in the tendency which the shortage of contraction produces in the portions (for example, opening part of a bottle, etc.) as which bigger contraction is required, for example. It is not less than 78% preferably. As for the heat shrinkage rate of the maximum shrinkage direction measured on condition of (B), it is preferred that it is 95% or less

[0026]

When the heat shrinkage rate (direction-crossing-at-a-right-angle heat shrinkage rate) of the direction which intersects perpendicularly with the maximum shrinkage direction measured on condition of (B) exceeds a mentioned range, the appearance defect by TATEHIKE cocurs. "TATEHIKE" is that the length of the label after contraction becomes irregular, and the appearance defect which draws the line where the upper bed edge of the label after making a PET bottle etc. carry out covering contraction curves downward, or draws the line where a lower end edge curves upward is said. As for the direction-crossing-at-a-right-angle heat shrinkage rate measured on condition of (B), it is preferred that it is 7% or less.

[0027]

In addition, the heat contraction nature polyester system film of this invention, The heat shrinkage rate of the measured maximum shrinkage direction on the above conditions (C) about the film before heat contraction  $X_0$  (%). When the heat shrinkage rate of the maximum shrinkage direction measured on the above conditions (C) is made into  $X_{10}$  (%) about the film to which the maximum shrinkage direction was made to once carry out heat contraction the film before heat contraction 10%, the heat shrinkage rate difference delta (%) expressed with an upper type (1) is not less than 10% of 20% or less. If the above-mentioned heat shrinkage rate difference delta is a heat contraction nature polyester system film which

becomes in a mentioned range, the heat contraction nature label which has a reinforcing effect of a covering container can be obtained.

[0028]

In the heat contraction nature label obtained from the heat contraction nature polyester system film which is less than a mentioned range, the above—mentioned heat shrinkage rate difference delta becomes insufficient [ the reinforcing effect of the container after covering contraction]. In the heat contraction nature polyester system film of this invention, the desirable heat shrinkage rate difference delta is 17% or less. Since the above—mentioned heat shrinkage rate  $X_{10}$  is a value measured using the film which carried out heat contraction 10%, the minimum of the heat shrinkage rate difference delta is not less than 10%.

[0029]

Incidentally with the usual heat contraction nature polyester system film. Once carrying out heat contraction 10%, the final heat shrinkage rate (sum total of 10% of the first heat shrinkage rate, and the 2nd heat shrinkage rate) at the time of carrying out heat contraction again, It falls more greatly than the heat shrinkage rate in the case of having shrunk the film before heat contraction thoroughly on the same heat contraction conditions (that is, the above-mentioned heat shrinkage rate difference delta will exceed a mentioned range). In the film of this invention, the presentation of the polyester used for a film is made suitable so that it may mention later, and it is supposed that the extension conditions of a film are controlled and the heat shrinkage rate difference delta in a mentioned range will be secured. [0030]

The above-mentioned "heat shrinkage rate of a maximum shrinkage direction" means the heat shrinkage rate in the direction which the sample contracted most, and a maximum shrinkage direction and direction crossing at a right angle are decided by the length of a square lengthwise direction or a transverse direction. A heat shrinkage rate (%) a sample (10 cm x 10 cm) by the heat shrinkage rate measured on condition of (A) in 70 \*\*\*\*0.5 \*\* warm water, In the heat shrinkage rate measured on condition of (B), in 85 \*\* \*\*\*0.5 \*\* warm water, The length of a film immediately after being immersed for 5 seconds and carrying out heat contraction according to no load condition into 95 \*\* \*\*\*0.5 \*\* warm water, respectively in heat shrinkage rate  $X_0$  measured on condition of (C), after being immersed in 25 \*\* underwater [ \*\*0.5 \*\*] for 10 seconds by no load condition, and the lateral length are

Heat shrinkage rate =100x(length after the length-contraction before contraction) / (length before contraction)

It is the value which was boiled, and was followed and calculated.

[0031]

measured, and it is a lower type.

The above-mentioned heat shrinkage rate X<sub>10</sub> used for calculation of the heat shrinkage

rate difference delta is measured as follows.

[0032]

First, the film made [ the maximum shrinkage direction ] to carry out heat contraction 10% is produced. The mold which counters and has two zippers is prepared so that only the end of the lot which a rectangular film counters can be grasped. A heat contraction nature polyester system film is judged in a square or a rectangle in parallel with a maximum shrinkage direction. The film after decision is fixed with a described [ above ] type. Immobilization is performed by slacking a film so that the both ends which intersect perpendicularly with the maximum shrinkage direction of this film may be grasped by a zipper and the film length between zippers and the ratio of the distance between zippers of a mold may be set to 1:0.9. Then, after immersing the film fixed to the mold for 5 seconds and carrying out heat contraction by no load condition into 95 \*\* \*\*0.5 \*\* warm water, promptly, by no load condition, it is immersed for 10 seconds in 25 \*\* underwater [ \*\*0.5 \*\*], and pulls up to it. This film is removed from a mold, attached groundwater is removed, and the film made [ the maximum shrinkage direction ] to carry out heat contraction 10% is obtained.

[0033]

A sample (10 cm  $\times$  10 cm) is judged from the obtained film, heat shrinkage rate  $X_{10}$  is measured using this sample by the same method as the above-mentioned heat shrinkage rate  $X_0$ , and the heat shrinkage rate difference delta is computed by an upper type (1). [0034]

As for each of time until it goes into a sample cutting process from the making process of the film made [ the maximum shrinkage direction ] to carry out heat contraction 10%, and time until it goes into the heat contraction process in the conditions of (C) from a sample cutting process, it is desirable to consider it as a short time as much as possible. When keeping the sample judged when the film made [ the maximum shrinkage direction ] to carry out heat contraction 10% was kept to a sample cutting process to a heat contraction process, it is in an atony state, and it places in the air and under the environment of 25 \*\* or less, and unnecessary heat contraction is kept from arising.

[0035]

The three-dimensional surface roughness Sdeltaa of the heat contraction nature polyester system film of this invention is 0.04 or less [ 0.008 or more ]. good film production nature and processability are secured by controlling Sdeltaa to such within the limits — things can be carried out. The three-dimensional surface roughness Sdeltaa can be measured with a three-dimensional roughness gauge (for example, Made in the Kosaka Factory "ET-30K"). [0036]

The three-dimensional surface roughness Sdeltaa is a three-dimensional average inclination, measures average inclination deltaa defined in this direction by the following

formula in rectangular directions about each 150 point set up in the arbitrary directions of a film at intervals of 2 micrometers by plane view, and says what averaged the measurement result in these all point. For example, what is necessary is to take the 150 above-mentioned points to the TD direction (they are rectangular directions to the running direction at the time of film manufacture) of a film, and just to measure average inclination deltaa about the MD directions (running direction at the time of film manufacture) of a film.

[Equation 1]

$$\Delta a = \frac{1}{L} \int_0^L \left| \frac{d}{dx} f(x) \right| dx$$

[0038]

Among [type, f(x) shows the profile curve and means the size (the time lower than positive and a mean line is made negative for the time higher than a mean line) of the unevenness in the coordinates x set up in the measurement direction in detail. L shows measurement length. 1

When Sdeltaa is too small, the performance traverse at the time of film manufacture falls, and there is a possibility that a crack may reach a film surface at the time of a run. On the other hand, if Sdeltaa is too large, the tear-proof nature of a film will get worse, and it will be generated by face powder at the time of a film run, and will become a cause of a printing omission. The minimum of more desirable Sdeltaa is 0.01, and a still more desirable minimum is 0.012. The maximum of more desirable Sdeltaa is 0.035 and a still more desirable maximum is 0.03.

[0039]

In addition, the three-dimensional surface roughness SRz of the heat contraction nature polyester system film of this invention is 0.6 micrometers or more 1.5 micrometers or less. The blocking resistance after container covering can be improved by controlling SRz within such limits. The three-dimensional surface roughness SRz can be measured like the above Sdeltaa with a three-dimensional roughness gauge (for example, Made in the Kosaka Factory "ET-30K").

[0040]

The three-dimensional surface roughness SRz is the ten three-dimensional average of roughness height, about each 150 point set up in the arbitrary directions of a film at intervals of 2 micrometers by plane view, measures the important average of roughness

height Rz in this direction in rectangular directions, and says what averaged a measurement result in these all point. For example, what is necessary is to take the 150 above-mentioned points to a TD direction (they are rectangular directions to a running direction at the time of film manufacture) of a film, and just to measure the ten-point average of roughness height Rz about MD directions (running direction at the time of film manufacture) of a film.

It becomes easy to block, when SRz was too small, manufacture a full label from a film, a container is made to carry out covering contraction for example, and this covering container is packed up in the hot state (packing etc.). On the other hand, if SRz is too large, the tear—proof nature of a film will get worse, and it will be generated by face powder at the time of a film run, and will become a cause of a printing omission. A minimum of more desirable SRz is 0.65 micrometer and a still more desirable minimum is 0.7 micrometer. A maximum of more desirable SRz is 1.3 micrometers and a still more desirable maximum is 1.0 micrometer.

Sdeltaa and SRz are controlled by a film of this invention in a mentioned range according to making lubricant contain.

#### [0043]

[0046]

As the above-mentioned lubricant, an inorganic particle (inorganic lubricant), organic salt particles, Polymer Division particles, etc. are mentioned. As an inorganic particle, carbonate (alkali carbonate earth metal salts, such as calcium carbonate, magnesium carbonate, and barium carbonate etc.), sulfate (sulfuric acid alkaline earth metal salt, such as barium sulfate etc.) and an phosphate (phosphoric acid alkaline earth metal salt, such as lithium phosphate.) Oxide stock particles (an aluminum oxide, oxidized silicon, titanium oxide, zirconium oxide, etc.), kaolin and talc, such as phosphoric acid alkaline earth metal salt, such as calcium phosphate and magnesium phosphate, lithium fluoride, etc. can be illustrated. Also in these, silica (oxidized silicon) particles are preferred. Especially a desirable silica particle is the floc which was able to condense and do primary particles. Such a silica particle is useful, although it has good handlability and a good film of transparency is obtained.

As organic salt particles, oxalates (oxalic acid alkaline earth metal salt, such as a calcium oxalate etc.) and terephthalic acid salt (alkaline earth metal salt, such as calcium salt, magnesium salt, and barium salt, zinc salt, manganese salt, etc.) are mentioned.

[0045]

As Polymer Division particles, vinyl system monomers, such as divinylbenzene, styrene, and acrylic acid (meta), are independent, or a copolymer, polytetrafluoroethylene, benzoguanamine resin, thermosetting urea resin, thermosetting phenolic resin, etc. are mentioned. Especially crosslinked polymer particles are preferred.

As for particle diameter of these lubricant, it is preferred that it is 0.01 micrometers or more 4 micrometers or less in mean particle diameter, and it is more preferred that it is [ 0.05 micrometer or more ] 3.5 micrometers or less. If it becomes difficult to make Sdeltaa more than the above-mentioned lower limit if mean particle diameter of lubricant is less than a mentioned range and mean particle diameter of lubricant exceeds a mentioned range, it will become difficult for below the above-mentioned upper limit to carry out SRz. Mean particle diameter of lubricant here is the nominal value of a lubricant maker, and is the mean particle diameter measured about particles which ground floc of primary particles and adjusted particle diameter.

### [0047]

As an addition of lubricant, it is recommended among the film whole quantity that more than 0.02 mass % adjusts [ below 0.5 mass %] so that below 0.4 mass % may become [ more than 0.03 mass %] more preferably. When a film has two or more layers so that it may mention later, in more than 0.02 mass %, content of lubricant to the layer whole quantity should just adjust [ below 0.5 mass %] for each class about two-layer [ which is located in the outermost surface ] so that below 0.4 mass % may become [ more than 0.03 mass %] more preferably. If it becomes difficult to make Sdeltaa more than the above-mentioned lower limit if an addition of lubricant is less than a mentioned range and an addition of lubricant exceeds a mentioned range, it will become difficult for below the above-mentioned upper limit to carry out Sdeltaa.

#### [0048]

In a heat contraction nature polyester system film of this invention. When a thermal-shrinkage-stress value about this direction of a film after carrying out heat contraction to a maximum shrinkage direction 10% is measured on with specimen 20 mm in width, and a distance between zippers of 100 mm conditions among a 5 m [ in temperature of 90 \*\*, and blow-off speed ]/second hot wind, it is preferred that a maximum-heat-shrinkage-stress value is 7 or more MPa. If the above-mentioned maximum-heat-shrinkage-stress value is a film of 7 or more MPa, a heat contraction nature label in which a reinforcing effect of a covering container was more excellent can be obtained. That is, the above-mentioned maximum-heat-shrinkage-stress value is in a tendency for an effect of reinforcing a covering container to fall, in a heat contraction nature label obtained from a film which is less than a mentioned range. As for the above-mentioned maximum-heat-shrinkage-stress value, it is more preferred that they are 10 or more MPa, and it is still more preferred that they are 11 or more MPa.

The above-mentioned maximum-heat-shrinkage-stress value is measured by the following methods

[1] From a heat contraction nature polyester system film, the length of a maximum

shrinkage direction cuts down a specimen which are 200 mm and 20 mm in width.

- [2] Heat inside of a heating furnace of a tension tester (for example, product made from an Oriental energy machine "tensilon") provided with a hot wind type heating furnace at 90 \*\*.

  [3] Stop air blasting and set a specimen in a heating furnace. Distance between zippers shall
- [3] Stop air blasting and set a specimen in a heating furnace. Distance between zippers shal be 100 mm (fixed), and the length between zippers of a specimen and distance between zippers slack a specimen, and set it so that it may be set to 1:0.9.
- [4] Shut a door of a heating furnace promptly and resume air blasting (5 m [ in temperature of 90 \*\*, and blow-off speed ]/second hot wind). Heat contraction of the specimen is carried out 10%, and thermal shrinkage stress after this heat contraction is detected and measured.
- [5] The maximum is read in a chart and let this be a maximum—heat—shrinkage—stress value (MPa).

[0050]

As for a heat contraction nature polyester system film of this invention, it is preferred that thickness is more uniform, and it is recommended that thickness distribution which specifies thickness displacement measurement in a maximum shrinkage direction of a film at an upper ceremony (2) when a specimen 50 cm in length and 5 cm in width is followed is 6% or less.

[0051]

Ten specimens which the above-mentioned thickness distribution is 50 cm in length and 5 cm in width, and make a maximum shrinkage direction of a film the length direction are created, About each specimen, a contact process thickness meter (for example, "KG60/A" by ANRITSU CORP.) is used, After measuring thickness of the length direction continuously, outputting to a chart, asking for maximum thickness, the minimum thickness, and average thickness from this output and computing thickness distribution using an upper type (2) from these, it is obtained by calculating average value of thickness distribution of ten specimens.

[0052]

In a film in which the above-mentioned thickness distribution exceeds 6%, it is presswork, printability at the time of printing a multicolor pattern especially is inferior, and when piling up two or more colors, it is easy to carry out raw [ of the gap ]. In order to manufacture a label from a film of this invention, when carrying out solvent bonding and tube—ization-processing it, superposition of an adhesion part of a film becomes difficult. When the above-mentioned thickness distribution rolls round to rolled form according to a film manufacturing process in a film exceeding 6%, a difference of partial volume hardness arises and slack and wrinkles of a film resulting from this occur, and also when it becomes impossible to use it as a heat contraction nature film, it is. 5% or less of the above-mentioned thickness distribution is still more desirable, and is desirable. [ especially

4% or less of ]

It is preferred that a melt resistivity value in 275 \*\* is below 0.70x10<sup>8</sup> omega—cm in a heat contraction nature polyester system film of this invention. Thus, if a melt resistivity value is small, it faces cooling a film which carried out melting extrusion from an extrusion machine with a casting roll, and the electrostatic adhesion of a film to a roll can be improved. Therefore, the stability of cooling solidification can be improved and casting speed (production rate) can be raised. As for a melt resistivity value, it is more preferred that it is below 0.65x10<sup>8</sup> omega—cm, and it is still more preferred that it is below 0.60x10<sup>8</sup> omega—cm. [0.054]

Film quality can also be raised, if a melt resistivity value is low and electrostatic adhesion is high. Namely, when electrostatic adhesion is low, cooling solidification of a film becomes imperfect, exhaust air enters locally between a casting roll and a film, and there is a possibility that a pinner bubble (stripe-like defect) may occur in a film surface, but. If excelled in electrostatic adhesion, generating of said pinner bubble can be reduced and film appearance can be made good.

[0055]

In addition, thickness of a film can be equalized, when a melt resistivity value is low enough and electrostatic adhesion is high enough. Namely, if electrostatic adhesion to a casting roll is low, thickness of a cast unstretched film original fabric will become uneven, and the heterogeneity of thickness will be expanded more in an oriented film which extended this unstretched film, but. When electrostatic adhesion is high enough, thickness can be equalized also in an oriented film.

[0056]

In order to control a melt resistivity value of a film to a mentioned range, it is desirable to make an alkaline earth metal compound and the Lynn content compound contain in a film. Although at least an alkaline earth metal compound can lower a melt resistivity value, if the Lynn content compound is made to live together, a melt resistivity value can be lowered remarkably. Although a Reason for the ability to reduce a melt resistivity value remarkably by combining an alkaline earth metal compound and the Lynn content compound is not clear, by making the Lynn content compound contain, quantity of a foreign matter can be decreased and it is presumed because quantity of a charge carrier can be increased. [0057]

As for content of an alkaline earth metal compound in a film, it is preferred to use more than 40 ppm (it is [ a mass basis and the following ] the same) on the basis of alkaline-earth-metals atom M², for example, it is more preferred to be referred to as not less than 50 ppm, and it is still more preferred to be referred to as not less than 60 ppm. When there is too little quantity of an alkaline earth metal compound, it is to lower a melt

resistivity value in a tendency which becomes difficult. Even if it increases content of an alkaline earth metal compound too much, a reduction effect of a melt resistivity value is saturated and it is in a tendency for evils, such as foreign matter generation and coloring, to become large rather. Therefore, as for content of an alkaline earth metal compound, it is preferred to be referred to as 400 ppm or less on the basis of alkaline-earth-metals atom  $M^2$ , for example, it is more preferred to be referred to as 350 ppm or less, and it is still more preferred to be referred to as 300 ppm or less.

[0058]

As for content of the Lynn content compound in a film, it is preferred to use more than 10 ppm (it is [ a mass basis and the following ] the same) on the basis of phosphorus atom P, for example, it is more preferred to be referred to as not less than 15 ppm, and it is still more preferred to be referred to as not less than 20 ppm. If there is too little quantity of the Lynn content compound, it may become difficult to fully lower a melt resistivity value, and a generated amount of a foreign matter cannot be reduced. Even if it increases content of the Lynn content compound too much, a reduction effect of a melt resistivity value will be saturated. Furthermore generation of a diethylene glycol is promoted, and since it is difficult to control the generated amount moreover, there is a possibility of differing from what film properties were planning. Therefore, as for content of the Lynn content compound, it is preferred to be referred to as 500 ppm or less on the basis of phosphorus atom P, for example, it is more preferred to be referred to as 400 ppm or less, and it is still more preferred to be referred to as 400 ppm or less.

[0059]

As for a mass ratio  $(M^2/P)$  of alkaline-earth-metals atom  $M^2$  in a film, and phosphorus atom P, when lowering a melt resistivity value of a film with an alkaline earth metal compound and the Lynn content compound, it is desirable that it is 1.5 (1.7 or more [ 1.6 or more / Preferably / still more preferably ]) or more. By making a mass ratio  $(M^2/P)$  or more into 1.5, a melt resistivity value can be reduced remarkably. If a mass ratio  $(M^2/P)$  exceeds 5.0, a generated amount of a foreign matter may increase, or a generated amount of a foreign matter may increase, or a film may color. Therefore, as for a mass ratio  $(M^2/P)$ , it is preferred to use 5.0 or less, it is more preferred to use 4.5 or less, and it is still more preferred to use 4.0 or less.

[0060]

In order to lower a melt resistivity value of a film further, it is desirable to make an alkali metal compound contain in a film in addition to the above-mentioned alkaline earth metal compound and the Lynn content compound. Even if it makes a film contain an alkali metal compound independently, it cannot lower a melt resistivity value, but it can lower a melt resistivity value remarkably by adding to a coexistence system of an alkaline earth metal compound and the Lynn content compound. Although it is not clear about the Reason, it is

presumed by forming a complex by three persons of an alkali metal compound, an alkaline earth metal compound, and the Lynn content compound that a melt resistivity value is lowered.

#### [0061]

Content of an alkali metal compound in a film, It is preferred to use more than 0 ppm (it is [ a mass basis and the following ] the same) on the basis of alkaline metal atom M¹, it is more preferred to be referred to as not less than 5 ppm, it is still more preferred to be referred to as not less than 6 ppm, and especially a thing set to not less than 7 ppm is preferred. Even if it increases content of an alkali metal compound too much, a reduction effect of a melt resistivity value is saturated and a generated amount of a foreign matter increases further. Therefore, as for content of an alkali metal compound, it is preferred to be referred to as 100 ppm or less on the basis of alkaline metal atom M¹, it is more preferred to be referred to as 90 ppm or less, and it is still more preferred to be referred to as 80 ppm or less.

As the above-mentioned alkaline earth metal compound, hydroxide of alkaline-earth metals, An alkoxide, an aliphatic-carboxylic-acid salt (preferably acetate, such as acetate and butyrate), an aromatic-carboxylic-acid salt (benzoate), salts (salt with phenol, etc.) with a compound which has a phenolic hydroxyl group, etc. are mentioned. As alkaline-earth metals, magnesium, calcium, strontium, barium (preferably magnesium), etc. are mentioned. Magnesium acetate is contained especially in a desirable alkaline earth metal compound magnesium hydroxide, magnesium methoxide, magnesium acetate, calcium acetate, strontium acetate, barium acetate, etc. The above-mentioned alkaline earth metal compound is independent, or it can be used, combining it two or more sorts.

As the above–mentioned Lynn content compound phosphoric acid (phosphoric acid, phosphorous acid, hypophosphorous acid, etc.). And the ester (alkyl ester, aryl ester, etc.) and alkyl phosphonic acid, aryl phosphoric acid, and those ester (alkyl ester, aryl ester, etc.) are mentioned. As desirable phosphorus compounds, it is aliphatic series ester (alkyl ester of phosphoric acid, etc.; for example) of phosphoric acid and phosphoric acid. Phosphoric acid mono–  $C_{1-6}$  alkyl ester, such as phosphoric acid monomethyl ester, phosphoric acid monoethyl ester, and phosphoric acid monobutyl ester, and phosphoric acid monobutyl ester, phosphoric acid and phosphoric acid Tori  $C_{1-6}$  alkyl ester, such as trimethyl phosphate ester, phosphoric acid tributyl phosphate ester, and tributyl phosphate ester, and tributyl phosphate ester etc., Aromatic ester (mono– \*\* JI or Tori  $C_{6-9}$  aryl ester of phosphoric acid, such as triphenyl phosphate and tricresyl phosphate, etc.) of phosphoric acid, aliphatic series ester of phosphorous acid (alkyl ester of phosphorous acid, etc.; for example) Mono– \*\* JI of phosphorous acid, such as phosphorous acid tributyl, or alkyl phosphonic acid ( $C_{1-6}$  alkyl phosphonic acid, such as

methylphosphonic acid and ethylphosphonic acid) and alkyl phosphonic acid alkyl ester (dimethyl methylphosphonate.), such as Tori  $C_{1-6}$  alkyl ester Mono- \*\*\*\* of  $C_{1-6}$  alkyl phosphonic acid, such as ethyl dimethyl phosphonate, JI  $C_{1-6}$  alkyl ester etc., aryl phosphonic acid alkyl ester (dimethyl phosphonate.) Mono- \*\*\*\* of  $C_{8-9}$  aryl phosphonic acid, such as diethyl phenylphosphonate, JI  $C_{1-6}$  alkyl ester etc., Aryl phosphonic acid, such as diethyl phenylphosphonate, JI  $C_{1-6}$  alkyl ester etc., Aryl phosphonic acid, such as diphenyl phenylphosphonate, is JI  $C_{6-9}$  aryl ester etc.) etc. can be illustrated. Phosphoric acid and phosphoric acid trialkyl (trimethyl phosphate etc.) are especially contained in the desirable Lynn content compound. These Lynn content compound is independent, or it can be used, combining it two or more sorts.

#### [0064]

As the above-mentioned alkali metal compound, hydroxide of an alkaline metal, carbonate, an aliphatic-carboxylic-acid salt (preferably acetate, such as acetate and butyrate), an aromatic-carboxylic-acid salt (benzoate), salts (salt with phenol, etc.) with a compound which has a phenolic hydroxyl group, etc. are mentioned. Lithium, sodium, potassium (preferably sodium), etc. are mentioned as an alkaline metal. Sodium acetate is contained especially in a desirable alkaline earth metal compound lithium hydroxide, sodium hydroxide, a potassium hydrate, lithium carbonate, sodium carbonate, potassium carbonate, lithium acetate, sodium acetate, sodium acetate, sodium acetate, potassium acetate.

### [0065]

A heat contraction nature polyester system film of this invention has an ester unit formed from a polyvalent carboxylic acid component and a polyhydric alcohol component as a main component unit.

#### T00661

As polyvalent carboxylic acid for forming a polyvalent carboxylic acid component in an ester unit, Aromatic dicarboxylic acid, such as terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid, and alt-phthalic acid; Adipic acid, Aliphatic dicarboxylic acid, such as azelaic acid, sebacic acid, and decane dicarboxylic acid; these ester formation derivatives, such as alicyclic dicarboxylic acid; are mentioned.

#### [0067]

When using above-mentioned aliphatic dicarboxylic acid, it is preferred that polyvalent carboxylic acid component 100 mol % Naka of a film and an aliphatic dicarboxylic acid component are less than [ 3 mol % ]. Although mentioned later for details, in order to demonstrate tear-proof nature, intensity, heat resistance, etc. in a heat contraction nature polyester system film of this invention, it is desirable to use an ethylene terephthalate unit as a main component unit. Therefore, although it is recommended that a terephthalic acid component serves as a subject, a polyvalent carboxylic acid component in a film, When the amount of aliphatic dicarboxylic acid components is more than 3 mol %, in a heat contraction

nature label obtained from this film, only rigidity (waist of a film) which can be equal to high-speed wearing in a container may not be obtained.

#### [0068]

As for the polyvalent carboxylic acid (for example, trimellitic acid, pyromellitic acid, these anhydrides, etc.) more than trivalent, not using is preferred. In a heat contraction nature polyester system film which has these polyvalent carboxylic acid components, sufficient heat shrinkage rate may become is hard to be acquired.

## [0069]

As a polyhydric alcohol class for forming a polyhydric alcohol component in an ester unit, in order to form an ethylene terephthalate unit, ethylene glycol is used. In addition, propylene glycol, 1,4-butanediol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, neopentyl glycol, Aliphatic series diol, such as 2-methyl-1,5-pentanediol and 2,2-diethyl-1,3-propanediol, Alicyclic diol, such as 1,4-cyclohexane dimethanol, dimer diol, a bisphenol compound, or alkylene oxide adduct of the derivative can be used together.

### [0070]

a film of this invention — diol (for example, propylene glycol.) of the carbon numbers 3-6 It is preferred to use one or more sorts and polyester which adjusted glass transition temperature (Tg) to 60-75 \*\* using 1,4-cyclohexane dimethanol among 1,4-butanediol, necoentyl glycol. 1.6-hexanediol, etc.

#### [0071]

It is desirable to use especially polyester which used neopentyl glycol together in respect of reservation of each of above—mentioned heat shrinkage rates, improvement in contraction result appearance, and container reinforcing effect reservation, polyhydric alcohol component % of 100 mol of a film — inside and a neopentyl glycol component amount — more than 15 mol % — it is more than 18 mol % preferably, and it is recommended less than 27 mol % and that it is less than 25 mol % preferably. moreover — a case where diol of carbon numbers 3–6 other than neopentyl glycol is used — polyhydric alcohol component % of 100 mol of a film — inside and these diol components — more than 3 mol % — it is more than 5 mol % preferably, and it is desirable less than 15 mol % and that it is less than 13 mol % preferably. In addition, in a case where 1 and 4–cyclohexane dimethanol is used. polyhydric alcohol component % of 100 mol of a film — inside and 1 and 4–cyclohexane dimethanol component amount — more than 15 mol % — it is more than 18 mol % preferably, and less than 27 mol % and using less than 25 mol % preferably are recommended.

## [0072]

As for diol (for example, octanediol etc.) of eight or more carbon numbers except a suitable polyhydric alcohol class of the above-mentioned illustration, and polyhydric alcohol more than trivalent, not using is preferred. In a heat contraction nature polyester system film which has these diol components and polyhydric alcohol components, sufficient heat

shrinkage rate may become is hard to be acquired.

[0073]

Although it is not a polyhydric alcohol class, a part of lactone represented by epsilon-caprolactone may be used. Lactone serves as a unit which carries out ring breakage and has an ester bond to both ends.

[0074]

If the tear-proof nature of a film, intensity, heat resistance, etc. are taken into consideration, it is preferred to choose so that component unit 100 mol % Naka of a heat contraction nature polyester system film and an ethylene terephthalate unit may become more than 50 mol %. Therefore, it is preferred to make more than 50 mol %, polyhydric alcohol component 100 mol % Naka, and an ethylene glycol component more than 50 mol % for polyvalent carboxylic acid component 100 mol % Naka and a terephthalic acid component (ingredient which consists of terephthalic acid or its ester). More than 55 mol % of an ethylene terephthalate unit is more preferred, and more than its 60 mol % is still more preferred.

Although polyester which constitutes a heat contraction nature polyester system film can be manufactured by carrying out melt polymerization with a conventional method, . Carry out the polycondensation of the oligomer by which the direct reaction of polyvalent carboxylic acid and the polyhydric alcohol class might be carried out. After carrying out the ester exchange reaction of what is called a direct polymerization method, and a methyl ester object and polyhydric alcohol of polyvalent carboxylic acid, what is called an ester interchange method etc. that carry out a polycondensation are mentioned, and arbitrary manufacturing methods can be applied. It may be polyester obtained by other polymerization methods. A degree of polymerization of polyester is made into intrinsic viscosity, and is preferred. [ of a thing of 0.3 – 1.3 dl/g ]

[0076]

As a polymerization catalyst, can use conventional various catalysts, and For example, a titanium system catalyst, An antimony system catalyst, a germanium system catalyst, a tin series catalyst, a cobalt system catalyst, Titanium system catalysts (titanium tetrabutoxide etc.), antimony system catalysts (antimonous oxide etc.), a germanium system catalyst, cobalt (diacid-ized germanium etc.) system catalysts (cobaltous acetate etc.), etc. are mentioned preferably a manganese system catalyst etc.

[0077]

An addition stage in particular of an alkali metal compound, an alkaline earth metal compound, and the Lynn content compound is not limited, Before an esterification reaction and during esterification, although it may be which stage from an end of esterification before a polymerization process start, under polymerization, and after a polymerization, it is from an end of esterification before a polymerization process start preferably to desirable

arbitrary stages after an esterification process, and a pan. If an alkaline earth metal compound and the Lynn content compound (and accepting necessity alkali metal compound) are added after an esterification process, a generated amount of a foreign matter can be reduced compared with a case where it adds before it.

[0078]

An antioxidant, an ultraviolet ray absorbent, a spray for preventing static electricity, colorant, an antimicrobial agent, etc. can also be added if needed.

[0079]

Although polyester film can be obtained by a publicly known method of mentioning later, In a heat contraction nature polyester system film, there are a method which performs copolymerization and carries out single use of this copolymerized polyester as a means to make two or more ingredients contain in a film, and a method which blends different gay polyester or copolymerized polyester of a kind.

[0800]

What is necessary is just to use copolymerized polyester obtained from a polyhydric alcohol class of a predetermined presentation, and the polyvalent carboxylic acid of a predetermined presentation in a method which carries out single use of the copolymerized polyester. In a method which blends polyester of a different presentation on the other hand, since the characteristic of a film can be easily changed only by changing a blend ratio and it can respond also to industrial production of a film of a various kind, it is preferably employable.

[0081]

It is preferred to specifically blend and use two or more sorts of polyester in which Tg(s) differ in the blending method. Polyester to blend may be three or more sorts.

[0082]

By blending and using two or more sorts of polyester, polyester does not dissolve but we are anxious about a trouble of a film milking, for example. However, an ester exchange reaction arose by being heated in a film extrusion process mentioned later, and as a result of polyester contained in a film turning into copolymerized polyester, it has usually become clear that troubles, such as the above-mentioned white blush mark, are avoided. Tg measured by a publicly known method about a film obtained from two or more sorts of polyester blends in which Tg(s) differ, for example can check copolymer-ization by such an ester exchange reaction from becoming a single value.

[0083]

As the addition method of lubricant used in order to make Sdeltaa and SRz into the above-mentioned predetermined value, How to supply and distribute in arbitrary stages of a polymerization process of polyester used as a film material; mix a polyester chip and lubricant which are obtained after a polymerization, carry out melting extrusion, and by

method; etc. which carry out chip making. A masterbatch chip which blended lubricant is produced beforehand and a method of performing film manufacture using this can adopt preferably. When blending two or more sorts of polyester chips and obtaining a film of this invention, there is no necessity of adding lubricant to a polyester chip of a complete range, for example, you may add only to one sort of polyester chips.

#### [0084]

It dries using dryers, such as a hopper dryer and a paddle dryer, or a vacuum dryer as a manufacturing method of a concrete film, and a raw material polyester chip is extruded to film state at temperature of 200-300 \*\* using an extrusion machine. Or an undried polyester raw material chip is similarly extruded to film state, removing moisture within a vent type extruder. On the occasion of extrusion, a T-die method, a tubular method, etc. may adopt any existing method. After extrusion is quenched and obtains an unstretched film. A film on which tension required for a film advance in a manufacturing process acted is also contained in an unstretched film here.

### [0085]

Although a film which consists of a single layer may be sufficient as a film of this invention, it may be a laminated film which laminated two or more layers (for example, two-layer, three layers, four etc. layers, etc.). When considering it as a laminated film, polyester of the same presentation as each class may be adopted, but it is also preferred to use polyester of a different presentation for every layer. In a case where it is considered as three layers, a central layer is also recommended having composition using polyester of other presentations using polyester of the presentations ame to both outer layers. In this case, although all the layers may contain the above-mentioned lubricant, it is also preferred to make it only the outermost layer (two layers located in the outermost surface) contain the above-mentioned lubricant. Although a laminating method in particular in a case of considering it as such a laminated film is not limited, a method of obtaining the above-mentioned unstretched film is employable by the publicly known co-extruding method etc., for example.

#### [0086]

As mentioned above, an electrode is allocated between the above-mentioned extrusion machine and a casting roll, voltage is impressed between an electrode and a casting roll, and it is recommended also in that sticking a film on a roll electrostatically attains equalization of thickness distribution of a film.

#### [0087]

Stretching treatment is performed to the above-mentioned unstretched film. After cooling by the above-mentioned casting roll etc., stretching treatment may be performed continuously, is once rolled round to rolled form after cooling, and is good in backward [ the ]. On productive efficiency, since it is practical that a maximum shrinkage direction is

the direction of film width (width), it shows an example of a method of extending in a case of making a maximum shrinkage direction into a transverse direction hereafter. Also when making a maximum shrinkage direction into the direction of film length (straight side), changing 90 degrees etc. can extend the extension direction in a following method according to normal operation.

#### [8800]

If it notes making thickness distribution of a heat contraction nature polyester system film equalize, and below the above-mentioned upper limit carrying out, When extending in a transverse direction using a tenter etc., it is preferred arrying out, when extending in a davance of a stretching process, and in this preheating process. It is preferred to heat until it reaches a certain temperature within limits whose film surface temperature is Tg+0 \*\*-Tg+60 \*\* at a low wind speed so that thermal conductance may become in below 0.00544 J/cm², sec, and \*\*\* (0.0013-calorie/cm², sec, and\*\*).

### [0089]

Lateral extension is performed with prescribed temperature of Tg-5 \*\*-Tg+15 \*\* within the limits. What is necessary is to divide extension into two or more steps, and just to perform it in a film of this invention, in order to carry out the above (A), a heat shrinkage rate of (B), and the heat shrinkage rate difference delta in a mentioned range and to carry out the above-mentioned maximum-heat-shrinkage-stress value in a mentioned range further. Hereafter, it explains taking the case of a case where it extends in two steps.

First, the 1st step of extensions are performed. Draw magnification is preferably made into 5.5 or less times 4.8 or more times 6.0 or less times 4.4 or more times to an unstretched film. The 1st step of extension temperature is made into the above-mentioned temperature (prescribed temperature of Tg-5 \*\*-Tg+15 \*\* within the limits).

#### [0091]

Next, it is preferred to perform heat setting, where a film is strained in the extension direction. Making a stress rate in that case into 5% or less not less than 2% preferably 6% or less 1% or more to a film after the 1st step of extensions is recommended. Heat setting temperature carries out [ about 1–5 \*\* / temperature / the 1st step of / extension] whether it is made the same as the 1st step of extension temperature in the above-mentioned temperature requirement, and, as for heat setting time, it is desirable for 3 or less seconds to take 1 second or more preferably 5 or less seconds 0.5 second or more. [0092]

Next, the 2nd step of extensions are performed. Draw magnification is made into 1.5 or less (preferably 1.3 or less times) times 1.1 or more times to a film after heat setting (after [ when not carrying out heat setting ] the 1st step of extensions). As for the 2nd step of extension temperature, it is preferred to carry out [ about 1–5 \*\* / temperature / heat

setting ] whether it is made the same as heat setting temperature in the above-mentioned temperature requirement.

[0093]

Then, applying stress slightly [ it is desirable and ] on a film, it cools and a heat contraction nature polyester system film is obtained. As for a stress rate at the time of cooling, it is preferred to consider it as 0.1 to 3% to a film after the 2nd step of extensions.

[0094]

When making a process of extension into a three-stage, it is desirable to put in the above-mentioned heat setting process between the 2nd step of extensions and extension of a three-stage eye. What is necessary is just to determine conditions of a heat setting process according to the above-mentioned heat setting conditions. What is necessary is just to also determine extension conditions of a three-stage eye according to the 2nd step of above-mentioned extension conditions.

[0095]

Since a design of extension equipment in industrial production becomes difficult from viewpoints of heat shrinkage rate control of a film, etc. when there are not much too many step numbers although more ones of a step number of extension are preferred, it is desirable to consider it as four or less steps preferably six or less steps.

[0096]

In this lateral orientation process, it is preferred to use equipment which can make change of film surface temperature small. Namely, although there are a preheating process before extension, a stretching process, a heat treatment process after extension, relaxing treatment, a re-stretching treatment process, etc. in a stretching process, It is preferred that the range of fluctuation of skin temperature of a film especially measured in an optional point in a preheating process, a stretching process, and a heat treatment process after extension is the mean temperature of less than \*\*1 \*\*, and it is still more desirable if it is less than \*\*0.5 \*\* in mean temperature. When the range of fluctuation of skin temperature of a film is small, it is to cover a film overall length, to be extended and heat—treated at the same temperature, and for the physical properties of a heat contraction action or others to equalize.

[0097]

As the method of extension, 1.1 times – 2.0 times as many extensions may be preferably given to not only width 1 axis extension by a tenter but a lengthwise direction 1.0 time – 4.0 times. Thus, when performing biaxial extension, any of biaxial extension and simultaneous biaxial extension may be sufficient one by one, and re-extension may be performed if needed. In biaxial extension, which methods, such as every direction, length-and-breadth, in every direction length, and length-and-breadth width, may be used as an order of extension one by one. Also in a case where these vertical stretching processes or a biaxial stretching

process is adopted, it is preferred like lateral orientation to make change of film surface temperature as small as possible in a preheating process, a stretching process, etc. [0098]

As equipment which can make small change of the above-mentioned film surface temperature, For example, in order to control a wind speed of a hot wind which heats a film, an inverter is attached, and equipment which can control change of a wind speed, equipment which uses low-pressure steam of 500 or less (below 5 kgf/cm²) kPa for a heat source, and can control a temperature change of a hot wind, etc. are mentioned. [0099]

As for a coefficient of heat transfer of a stretching process, if a point which controls internal generation of heat of a film accompanying extension, and makes crosswise film temperature spots small is noted, it is preferred to use more than 0.00377 J/cm², sec, and \*\* (0.0009-calorie/cm², sec, and\*\*). 0.00544 - 0.00837 J/cm², sec, and \*\*

(0.0013−0.0020−calorie/cm², sec, and\*\*) are more preferred.

[0100]

Although thickness in particular of a heat contraction nature polyester system film of this invention is not limited, as a heat contraction nature polyester system film for labels, 10–100 micrometers is preferred and 20–60 micrometers is still more preferred, for example.

[0101]

Even if it uses a heat contraction nature label obtained using a heat contraction nature polyester system film of this invention for full labels (label that high contraction is required selectively), such as a PET bottle, it can present good contraction result appearance. It can become high contraction by short—time processing. It also has an effect of reinforcing containers, such as a PET bottle by which covering contraction was carried out. [0102]

In order to use the above—mentioned heat contraction nature polyester system film as a heat contraction nature label, For example, it takes out, after carrying out predetermined time storage of the heat contraction nature film before contraction into environment which controlled temperature and humidity, Using publicly known tube shape molding equipment, a film is rounded off promptly, and an end is piled up, and it pastes [ a solvent for adhesion is applied inside with prescribed width for a while from the edge of one side of a film piece end, and ] up, and is processed into a tube. This tube can be cut out to predetermined length and it can be considered as a heat contraction nature label of this invention.

[0103]

As for adhesion of a film, although it is also possible to adopt a melt adhesion method to which melting of a part of film is carried out, it is preferred to carry out from a viewpoint of controlling change of the heat contraction characteristic of a label, etc., using a solvent. As a solvent which can be used, for example Benzene, toluene, xylene, Aromatic hydrocarbon,

such as trimethyl benzene; although organic solvents, such as oxo orchid species [, such as franc;1,3-dioxolanes, such as phenols; tetrahydrofurans, such as halogenated hydrocarbon; phenol such as a methylene chloride and chloroform, ];, are mentioned, Especially,

1.3-dioxolane is desirable at a point that safety is high.

[0104]

After equipping containers, such as a PET bottle, with the above-mentioned heat contraction nature label, heat contraction of it can be carried out and it can be made to cover with publicly known heat contraction means (a hot wind tunnel, a steam tunnel, etc.) which were mentioned above.

[0105]

Even if weight is about 30% lower than the conventional PET bottle, a PET bottle which carried out covering contraction of the heat contraction nature label of this invention is reinforced, for example to such an extent that it can be dealt with like the conventional PET bottle, for example in the cases, such as transportation and sale. It is preferred that not less than 75% of drum section surface area of a PET bottle is covered with a label in this case. [0106]

For example, in a label produced from a heat contraction nature film of this invention by performing it as follows, preferably, a diameter rate of change of a bottle measured by an after-mentioned method is 7% or less more preferably, and can demonstrate an outstanding container reinforcing effect 10% or less.

[0107]

[0108]

After applying 1,3-dioxolane inside by 3\*\*1-mm width for a while from the edge of one side of one end of a film (coverage: 3.0\*\*0.3g/mm²) and piling up this end, it judges in 14 cm in length, and size 6.7 cm in diameter, and a cylindrical label is obtained. It seals, after filling up a 500mL round shape PET bottle [21 cm in height, and center-section (drum section) 6.5 cm in diameter] with a mass of 20.5 g with water of 500mL, and this is equipped with the above-mentioned cylindrical label, a steam tunnel with a zone temperature of 85 \*\* is passed in 2.5 seconds, and this label is shrunk. Thus, a path (W<sub>1</sub>) of a bottle center section when "straw graph V10-C" by an Oriental energy machine company is used for a side center section the label covering bottle obtained and 15 kg of load is imposed on it by compressed mode is measured, and a diameter rate of change of a bottle (%) is searched for according to a following formula.

Diameter rate of change of a bottle (%) =100x( $W_1$ - $W_2$ )/ $W_2$ Here,  $W_2$  is a path of a bottle center section before imposing load.

Since it is easy to transform this container and may become causes, such as plugging, in a label that the above-mentioned diameter rate of change of a bottle exceeds 10% when a covering container falls, for example within a vending machine, it is not desirable.

[Example]

[0109]

Hereafter, although this invention is further explained in full detail according to working example, following working example does not restrict this invention, and when carrying out change implementation in the range which does not deviate from the meaning of this invention, it is included in this invention. "ppm" used by this example is a mass basis. The measuring method of the physical properties of the film obtained by working example and a comparative example is as follows.

[0110]

(1) Heat shrinkage rate

Cut out a film in square of 10 cm x 10 cm, and in the warm water of the temperature of following (A), (B), and (C), After being immersed for 5 seconds and carrying out heat contraction by no load condition, it is made to be immersed in 25 \*\* underwater [ \*\*0.5 \*\* ] for 10 seconds, and it pulls out from this underwater ones, the length of a sample and lateral length are measured, and it asks according to a following formula.

Heat shrinkage rate (%) =100x(length after the length-contraction before contraction) / (length before contraction)

Here, they are (A):75 \*\*\*\*0.5 \*\*, (B):85 \*\*\*\*\*0.5 \*\*, and (C):95\*\*0.5 \*\*. Let a direction with the largest contraction be a maximum shrinkage direction.

[0111]

(2) Heat shrinkage rate difference

The mold which counters and has two zippers is prepared so that only the end of the lot which a rectangular film counters can be grasped. A heat contraction nature polyester system film is judged in a square or a rectangle in parallel with a maximum shrinkage direction. The film after decision is fixed with a described [above] type. Immobilization is performed by slacking a film so that the both ends which intersect perpendicularly with the maximum shrinkage direction of this film may be grasped by a zipper and the film length between zippers and the ratio of the distance between zippers of a mold may be set to 1:0.9. Then, after immersing the film fixed to the mold for 5 seconds and carrying out heat contraction by no load condition into 95 \*\* \*\*0.5 \*\* warm water, promptly, by no load condition, it is immersed for 10 seconds in 25 \*\* underwater [ \*\*0.5 \*\* ], and pulls up to it. This film is removed from a mold, attached groundwater is removed, and the film made [ the maximum shrinkage direction ] to carry out heat contraction 10% is obtained. Then, in the state of an atony, this film is placed in the air and under the environment of 25 \*\* or less, and the following process is presented as much as possible with it for a short time.

[0112]

Judge this film in square of 10 cm x 10 cm, and in 95\*\*0.5 \*\* warm water, After being immersed for 5 seconds and carrying out heat contraction by no load condition, it is made to

be immersed in 25 \*\* underwater [ \*\*0.5 \*\*] for 10 seconds, and it pulls out from this underwater one, the length of a sample and lateral length are measured, and it asks for heat shrinkage rate  $X_{10}$  of a maximum shrinkage direction according to the above-mentioned heat shrinkage rate formula. The heat shrinkage rate of the maximum shrinkage direction called for on condition of (C) of the above (1) is made into  $X_0$ . From these values, the heat shrinkage rate difference delta (%) is computed according to an upper type (1).

(3) The three-dimensional surface roughness Sdeltaa, SRz

The sensing pin (measurement length: 1 mm, cutoff value:0.25mm) of the surface of a sample film is carried out along the MD directions of a film. A sensing pin type three-dimensional roughness gauge (Made in the Kosaka Factory "ET-30K") is used for a sensing pin (the radius of a needle: 2 micrometers, load:30mg). Length obtained by this sensing pin: Divide a 1-mm concavo-convex profile into 500 points in a 2-micrometer pitch, and make the height of each point incorporate into a three-dimensional granularity analysis device (Made in the Kosaka Factory "AT-30K").

[0114]

the same operation as the above is continuously performed to the TD direction of a film at intervals of 2 micrometers 150 times (namely, — continuing for 0.3 micrometer in the TD direction of a film). And Sdeltaa and SRz are calculated by making the above-mentioned analysis device calculate.

[0115]

(4) Maximum-heat-shrinkage-stress value

It measures using a tension tester with a heating furnace (the "tensilon" by Oriental energy machine incorporated company). From the film before heat contraction, at 200 mm, start a 20-mm-wide sample, and the length of a maximum shrinkage direction stops air blasting of the tension tester beforehand heated at 90 \*\*, makes a sample the distance between zippers of 100 mm, and it The length between zippers of a specimen, After the distance between zippers slacks a specimen and attaches it so that it may be set to 1:0.9, The door of a heating furnace is shut promptly, the contraction stress detected in a 5 m [ in (temperature of 90 \*\* and blow-off speed]/second hot wind when supply) is started from the three way of the back, the left, and the right is measured, and the maximum-heat-shrinkage-stress value (MPa) after 10% contraction is calculated from a measurement chart.

[0116]

(5) Thickness distribution

Ten specimens which make the maximum shrinkage direction of a film the length direction are created at 50 cm in length, and 5 cm in width, About each specimen, contact process thickness meters, such as for example, "KG60/A" (by ANRITSU CORP. etc.), are used, The thickness of the length direction is measured continuously and it outputs to a chart, and from this output, after asking for maximum thickness, the minimum thickness, and average thickness and computing thickness distribution using an upper type (2) from these, the average value of the thickness distribution of ten specimens is calculated, and it is considered as the thickness distribution of a film.

[0117]

(6) Melt resistivity value

The electrode plate of a couple is inserted into the sample (film) fused at the temperature of 275 \*\*, and the voltage of 120V is impressed. The current in that case is measured and melt resistivity value Si (ohm-cm) is computed based on a lower type.

Si=(A/I)x(V/io)

here — area [ of A:electrode ] (cm²), and Linter electrode distance (cm) V:voltage (V), and io: — it is current (A).

[0118]

(7) Contraction result nature

3 color prints are carried out to a film in the green by TOYO INK MFG. CO., LTD., and golden and white ink, It takes out, after keeping it for 250 hours in the environment controlled to the temperature of 30\*\*1 \*\*\*, and 85\*\*2\*\* of relative humidity, Using tube shape molding equipment, 1,3-dioxolane is applied inside by 3\*\*1-mm width for a while from the edge of one side of one end of a film (coverage: 3.0\*\*0.3g/mm³), and a film is rounded off promptly, and an end is piled up, and it pastes up, is considered as a tube, and rolls round in the state where it crushed level. This tube is cut out and it is considered as a cylindrical label 14 cm in height, and 6.7 cm in diameter. 500mL round shape PET bottle [21 cm in height made to fill up this label with water. Center-section (drum section) 6.5-cm] is equipped, the label whole quantity is passed for under the steam tunnel by FUJI ASTEC Co., Ltd. (SH-1500-L) on conditions with a zone temperature of 85 \*\* for tunnel pass time 2.5 seconds, and a label is shrunk (n= 20). [ in diameter ] The grade of a contraction result is judged visually and contraction result nature is evaluated in two steps. Generating nothing, x:wrinkles, a jump, or the shortage of contraction considers as generating all in which the standard of O.wrinkles, a jump, and contraction is insufficient.

[0119]

(8) Container reinforcing effect

Using tube shape molding equipment, 1,3-dioxolane is applied inside by 3\*\*1-mm width for a while from the edge of one side of one end of a film (coverage: 3.0\*\*0.3g/mm²), and a film is rounded off promptly, and an end is piled up, and it pastes up, is considered as a tube, and rolls round in the state where it crushed level. This tube is cut out and it is considered as a cylindrical label 14 cm in height, and 6.7 cm in diameter. Mass: It seals, after filling up a 20.5-g 500mL round shape PET bottle [21 cm in height, and center-section (drum section)

6.5 cm in diameter] with the water of 500mL, This is equipped with the above-mentioned cylindrical label, the label whole quantity is passed for under the steam tunnel by FUJI ASTEC Co., Ltd. (SH-1500-L) on conditions with a zone temperature of 85 \*\* for tunnel pass time 2.5 seconds after that, and a label is shrunk.

[0120]

Thus, the path  $(W_i)$  of a bottle center section when "straw graph V10-C" by an Oriental energy machine company is used for the side center section of the label covering bottle obtained and 15 kg of load is imposed on it by compressed mode is measured, and the diameter rate of change of a bottle (%) is searched for according to a following formula. Diameter rate of change of a bottle (%) =100x $(W_i-W_2)/W_2$ 

Here, W<sub>2</sub> is a path of the bottle center section before imposing load.

[0121]

(9) Blocking resistance

In the hot state immediately after this examination, all the label covering PET bottles obtained by the above-mentioned contraction result sex test are boxed one by one in a carton box (3x4=12 set) so that labels may contact. It takes out, after keeping this carton box for 24 hours to the interior of a room controlled at 40\*\*1 \*\*, and a three-stage estimates the grade of blocking of labels. although there is [Oblocking nothing and \*\*\*blocking ] a valuation basis, when it exfoliates, marks do not remain — there is x-blocking, and if it exfoliates, marks will remain — it comes out, and it is and O and \*\* are considered as success.

[0122]

(10) Performance traverse and tear-proof nature of a film

a film — width: — a slit is carried out to 100 mm and length:100m, and it is considered as tape shape. It connects with the roll for rolling up, after building the metal guide rolls which pull out a tape and are located in a line at intervals of 0.2 m from this roll after rolling round this tape and considering it as a roll. Then, it is made to run these all tapes by a part for speed:100-m/, and rolls round on the roll for rolling up. The quantity of the face powder by which it is generated on the quantity and the guide roll surface of an abrasion of a tape surface after a run is observed visually, and it evaluates in accordance with the following standard.

[0123]

[Performance traverse]

1: there is a 3:abrasion with many 2:abrasions with quite many abrasions a little -- 4: -- most abrasions -- nothing and 5:abrasion generating nothing,

[Tear-proof nature]

1: generating of face powder — extraordinary — many generating of 2-face powder — many generating of 3-face powder — hello, with no generating of \*\*\*, the generating \*\*\*\*\* nothing

of 4:face powder, and 5:face powder.

[0124]

The synthetic example 1

Between esterification reactions, as polyvalent carboxylic acid, dimethyl terephthalate 100 mol %, Ethylene glycol 100 mol % is taught by 2.2 times (mole ratio) to polyvalent carboxylic acid as a polyhydric alcohol class, Temperature up was carried out to 230 \*\*, having taught simultaneously and agitating antimonous oxide to polyvalent carboxylic acid, as a catalyst, so that it may be set to 81 ppm by Mg atom conversion 0.04-mol% to the polyester which has magnesium acetate 4 hydrate formed, and the ester exchange reaction was performed by ordinary pressure for 120 minutes. The end of the ester exchange reaction was considered as the place which methanol of the specified quantity distilled off. The polycondensation reaction was performed for about 40 minutes, and the polyester A was obtained after the end of an ester exchange reaction until a temperature raising and melt viscosity became 7000 poise to 280 \*\*, decompressing [ added so that it might be set to 58 ppm to the polyester formed by P atom conversion, and ] trimethyl phosphate over 85 minutes.

[0125]

The synthetic examples 2-7

The polyester B-G shown in Table 1 was compounded like the synthetic example 1. In the synthetic examples 2 and 3, as a polymerization catalyst, antimonous oxide was used so that Sb atoms might be set to 160 ppm to polyester, and the polyester B and C was obtained. In the synthetic example 4, as a polymerization catalyst, titanium tetrabutoxide was used so that Ti atoms might be set to 90 ppm to polyester, and the polyester D was obtained. Furthermore, in the synthetic example 6, cobaltous acetate 4 hydrate is made for Mg atom to be set to 20 ppm to polyester as a polymerization catalyst, further, titanium tetrabutoxide was used so that Ti atoms might be set to 15 ppm to polyester, and the polyester F was obtained. In the synthetic example 7, it presupposed that it is the same as that of the synthetic example 1 about a polymerization catalyst, and the polyester G was obtained.

[0126]

Polyester A-G obtained in the above-mentioned synthetic examples 1-7 is shown in Table 1. The inside of Table 1, DMT:dimethyl terephthalate and DMN:dimethyl naphthalate, EG:ethylene glycol, NPG:neopentyl glycol, BD:1,4-butanediol, CHDM:1,4-cyclohexane dimethanol, PPG: It is a propanediol.

[0127]

[Table 1]

|       | _                    | _    | _   | _   | _   | _   | <del></del> | Γ-  | _   |
|-------|----------------------|------|-----|-----|-----|-----|-------------|-----|-----|
|       |                      | PPG  | 1   | 1   | 1   | ı   | ı           | 1   | 100 |
|       | モル%)                 | CHDM | 1   | ı   | 1   | Ī   | I           | 30  | ı   |
|       | 多価アルコール類(モル%)        | BD   | 1   | ı   | ı   | 100 | ı           | ı   | 1   |
| 仕込み組成 | め笛アル                 | NPG  | 1   | 30  | 40  |     | ı           | 1   |     |
| 仕込    |                      | EG   | 100 | 70  | 09  | I   | 100         | 70  | ı   |
|       | 酸類(モル%)              | DMN  | 1   | 1   | ı   | 1   | 100         | ı   | 1   |
|       | ポリエステル 多価カルボン酸類(モル%) | DMT  | 100 | 100 | 100 | 100 | ı           | 100 | 100 |
|       | ポリエステル               |      | ٧   | Ф   | ၁   | D   | Э           | ь   | Ø   |

## [0128]

About lubricant, in the polyester A or the polyester E, We decided to manufacture beforehand the masterbatch which did 0.7 mass % addition of the silica (made by Fuji SHIRISHIA "SAISHIRIA 350") whose mean particle diameter is 1.8 micrometers as inorganic lubricant, the silica whose mean particle diameter is 0.007 micrometer, or the silica whose mean particle diameter is 5.80 micrometers, and to add on a film. Manufacture of the polyester A or the polyester E which blended the above-mentioned silica was performed by

making ethylene glycol distribute the above-mentioned silica in the case of these polymerizations. Incidentally, the silica in each film except the below-mentioned film No.5 (experiment 5) is introduced with the silica combination polyester A, and the silica in film No.5 is introduced with the silica combination polyester E.

[0129]

Experiment 1

The polyester A which carried out predrying separately, respectively, the silica combination polyester A. After mixing each chip of the polyester chip B and the polyester D at a rate shown in Table 2, it guenched with the casting roll melt extruding (T die) and after that at 280 \*\* using the single screw extruder, and the 260-micrometer-thick unstretched film was obtained. After preheating this unstretched film for 3 seconds at 100 \*\*, it extended in the transverse direction (film width direction) by the tenter, First, extension is extended 4.75 times at 77 \*\* (the 1st step), subsequently was strained 3% to the film width at the time of the end of the 1st step for 5 seconds at 77 \*\* (heat setting), subsequently it is 75 \*\*, and was extended by 1.1 times the film width at the time of the end of heat setting (the 2nd step), and was performed. Subsequently, it cooled to the film width at the time of the 2nd step of ends of extension, applying 1% of stress, and 50-micrometer-thick polyester system film No.1 was obtained. The evaluation result of the obtained film is shown in Tables 4 and 5. [0130]

### Experiment 2

The mixture ratio of the polyester chip was changed as shown in Table 2, and also the 260-micrometer-thick unstretched film was obtained like the experiment 1. About this unstretched film, it extended like the experiment 1 and 50-micrometer-thick polyester system film No.2 was obtained. The evaluation result of the obtained film is shown in Tables 4 and 5

[0131]

#### Experiment 3

The mixture ratio of the polyester chip was changed as shown in Table 2, and also the 260-micrometer-thick unstretched film was obtained like the experiment 1. About this unstretched film, it changed into the conditions shown in Table 3, and also extended like the experiment 1, and 50-micrometer-thick polyester system film No.3 was obtained. The evaluation result of the obtained film is shown in Tables 4 and 5.

[0132]

#### Experiment 4

The mixture ratio of the polyester chip was changed as shown in Table 2, and also the 260-micrometer-thick unstretched film was obtained like the experiment 1. About this unstretched film, it changed into the conditions shown in Table 3, and also extended like the experiment 1, and 50-micrometer-thick polyester system film No.4 was obtained. The

evaluation result of the obtained film is shown in Tables 4 and 5.  $\lceil 0.133 \rceil$ 

Experiment 5

The mixture ratio of the polyester chip was changed as shown in Table 2, and also the 260-micrometer—thick unstretched film was obtained like the experiment 1. About this unstretched film, it changed into the conditions shown in Table 3, and also extended like the experiment 1, and 50-micrometer—thick polyester system film No.5 was obtained. The evaluation result of the obtained film is shown in Tables 4 and 5.

[0134]

Experiment 6

The mixture ratio of the polyester chip was changed as shown in Table 2, and also the 260-micrometer-thick unstretched film was obtained like the experiment 1. About this unstretched film, it changed into the conditions shown in Table 3, and also extended like the experiment 1, and 50-micrometer-thick polyester system film No.6 was obtained. The evaluation result of the obtained film is shown in Tables 4 and 5.

[0135]

Experiment 7

The mixture ratio of the polyester chip was changed as shown in Table 2, and also the 260-micrometer—thick unstretched film was obtained like the experiment 1. About this unstretched film, it changed into the conditions shown in Table 3, and also extended like the experiment 1, and 50-micrometer—thick polyester system film No.7 was obtained. The evaluation result of the obtained film is shown in Tables 4 and 5.

Experiment 8

Lamination polyester system film No[ of three layers ].8 which consists of both outer layers and a central layer was obtained. Each chip of the polyester A polyester C and the polyester D which carried out predrying separately, respectively was mixed and used for the central layer at a rate shown in Table 2. Each chip of the polyester A, the silica combination polyester A, and the polyester F which carried out predrying separately, respectively was mixed and used for both outer layers at a rate shown in Table 2. These mixed polyester chips were quenched with the casting roll a co-extrusion and after that at 280 \*\* using the single screw extruder which has a T die, and the thickness of both outer layers obtained the unstretched film of the three-tiered structure whose thickness of 65 micrometers and a central layer is 130 micrometers, respectively. It changed into the conditions shown in Table 3 about this unstretched film, and also extended like the experiment 1, and lamination polyester system film No.8 which is 50 micrometers in thickness (the thickness of 12.5 micrometers and a central layer is 25 micrometers, respectively in the thickness of both outer layers) was obtained. The evaluation result of the obtained film is shown in Tables 4

and 5.

[0137]

Experiment 9

The mixture ratio of the polyester chip was changed as shown in Table 2, and also the 260-micrometer-thick unstretched film was obtained like the experiment 1. About this unstretched film, it changed into the conditions shown in Table 3, and also extended like the experiment 1, and 50-micrometer-thick polyester system film No.9 was obtained. The evaluation result of the obtained film is shown in Tables 4 and 5.

Experiment 10

The mixture ratio of the polyester chip was changed as shown in Table 2, and also the 260-micrometer—thick unstretched film was obtained like the experiment 1. About this unstretched film, it changed into the conditions shown in Table 3, and also extended like the experiment 1, and 50-micrometer—thick polyester system film No.10 was obtained. The evaluation result of the obtained film is shown in Tables 4 and 5.

[0139]

Experiment 11

The mixture ratio of the polyester chip was changed as shown in Table 2, and also the 260-micrometer—thick unstretched film was obtained like the experiment 1. About this unstretched film, it changed into the conditions shown in Table 3, and also extended like the experiment 1, and 50-micrometer—thick polyester system film No.11 was obtained. The evaluation result of the obtained film is shown in Tables 4 and 5.

[0140]

[Table 2]

|  |            | _      |      |    |    | ポリエステ | ポリエステル混合組成(質量部 | 戊(質量部) |     |    | シリ           | シリカ粒子        |
|--|------------|--------|------|----|----|-------|----------------|--------|-----|----|--------------|--------------|
| 15   15   15   16   17   10   10   10   10   10   10   10  |            | 中      | 成    | ٧  | æ  | ၁     | ۵              | ш      | ls. | g  | 平均粒径<br>(μm) | 添加量<br>(質量%) |
| 単層     10     80     一     10     -     -     -       車層     15     80     一     5     一     -     -       車層       工事層       TS       工事層       TS  | 1/LANo. 1  | (亩     | Mar. | 15 | 75 | -     | 10             | 1      | 1   | 1  | 1.80         | 0.04         |
| 華富     15     80     —     5     —     —       華富  | NLANO. 2   | 南      |      | 10 | 80 | ı     | 10             | ı      | ı   | 1  | 1.80         | 0.04         |
| 華富     15     16     17     17     17     17     17     17     17     17     17     17     17     17     17     17     18  | NYTHANO. 3 | 南      | 180  | 15 | 80 | 1     | 5              | 1      | ı   | ŀ  | 1.80         | 0.04         |
| # 層     一 <td>NLANO. 4</td> <th>東</th> <td>150</td> <td>15</td> <td>ı</td> <td>75</td> <td>10</td> <td>ı</td> <td>1</td> <td>   </td> <td>1.80</td> <td>0.04</td>  | NLANO. 4   | 東      | 150  | 15 | ı  | 75    | 10             | ı      | 1   |    | 1.80         | 0.04         |
| 単層     15     一     一     一     一     一     日       3階階     15     一     75     一     一     一       15     一     75     一     一     一       15     一     一     一     一     一       16     16     一     50     10     一       16     75     一     10     一     一       16     75     10     一     一     一       16     75     11     一     一     一  | NLANO. 5   | (東     | 180  | 1  | ı  | -     | 15             | 85     | ı   | ı  | 1.80         | 0.04         |
| 単層     15     一     一     一     一     一     一       3階論     雨外層     15     一     一     一     一       単層     40     一     50     10     一     一       単層     15     75     一     一     一       中層     16     75     一     一     一       中層     15     75     一     10     一   | 11.4No. 6  | (東     | EQU. | 15 | ı  | ı     | ı              | ı      | 85  | 1  | 1.80         | 90.0         |
| 中心層     15     一     75     10     一     一       南外層     15     一     一     一     85       単層     40     一     50     10     一     一       単層     15     75     一     10     一     一       単層     15     75     一     11     一     一   | JLANo. 7   | 甫      |      | 15 | 1  | 75    | 1              | 1      | 1   | 10 | 1.80         | 0.04         |
| Action 15     Action 16     Acti |            | 四年間の   | 中心層  | 15 | 1  | 75    | 10             | i      | 1   |    | 1            | ı            |
| 単層 40 50 10  | -          | MINIM. | 両外層  | 15 | 1  | -     | ı              | 1      | 85  | 1  | 1.80         | 0.04         |
| 単層 15 75 10 HB 15 75 11  | JLANO. 9   | 東      | H    | 40 | .1 | 50    | 10             | ı      | ı   | ı  | 1.80         | 0.06         |
|  | JL ANO. 10 | 南      | 191  | 15 | 75 |       | 10             | ı      | 1   | ı  | 0.007        | 1.00         |
|  | 1L 4No. 11 | (前     | 150  | 15 | 75 | 1     | 11             | 1      | 1   | ı  | 5.80         | 0.04         |

[0141]

When silica is blended with the layer which constitutes a film or a film in Table 2, The quantity of the polyester A expresses the amount of polyester A chips, and the total quantity of the polyester A in a silica combination polyester A chip, and the quantity of the polyester E expresses the amount of polyester E chips, and the total quantity of the polyester E in a silica combination polyester E chip. As for the case of 3 layered films, in the case of the monolayer film, the "silica particle" shows content [ as opposed to each outermost layer whole quantity for the content to the film whole quantity ], respectively. [0142]

[Table 3]

|      | が世帯の   | 緊急 (%)     | -          | -          | -          | 0          | -          | -          | _          | -            | 0          | -           | -              |
|------|--------|------------|------------|------------|------------|------------|------------|------------|------------|--------------|------------|-------------|----------------|
|      | 设階目    | 遺(い)       | 75         | 75         | 78         | 78         | 75         | 75         | 75         | 75           | 77         | 75          | 75             |
|      | 延伸2段階目 | 帝(明)       | 1.1        | 1.1        |            | 1.1        | 1.1        | 1.1        | 1.1        | 1.1          |            | 1.1         | 1.1            |
| 条件   |        | 聖聖(金)      | 2          | D          | ល          | ı          | ß          | ß          | Ŋ          | ω            | ı          | മ           | 2              |
| 延伸条件 | 熱固定    | 温度<br>(°C) | 77         | 77         | 80         | ı          | 75         | 75         | 77         | 75           | ı          | 77          | 77             |
|      |        | 緊張率 (%)    | ၉          | 3          | 3          | 0          | က          | က          | 3          | ဗ            | 0          | 8           | 9              |
|      | 设階目    | 過度<br>(%)  | 77         | 77         | 80         | 78         | 92         | 80         | 77         | 78           | 84         | 77          | 77             |
|      | 延伸1段階目 | 倍率<br>(倍)  | 4.75       | 4.75       | 4. 75      | 4.75       | 4.75       | 4.75       | 4.75       | 4.75         | 4.75       | 4.75        | 4.75           |
|      |        |            | 741LANO. 1 | 741L4No. 2 | 741L4No. 3 | 7416 Ao. 4 | 74114No. 5 | 7116 No. 6 | 741LLNo. 7 | 741L LANO. 8 | 741LLNo. 9 | 741L LIO 10 | 741L LIONO. 11 |

## [0143]

The draw magnification at the time of the 1st step of extensions the ratio to film width, and the stress rate in the case of heat setting among Table 3, A ratio [ as opposed to the film width after heat setting (after / when not carrying out heat setting / the 1st step extension) in the ratio to the film width after the 1st step of extensions and the draw magnification at the time of the 2nd step of extensions], and the stress rate at the time of cooling are ratios to the film width after the 2nd step of extensions. The stress rate "O%" of heat setting as used in film No.4, and 9 and 10 means having cooled the film, without the stress rate at the

time of cooling "0%" applying stress for not having established the heat setting process after the 2nd step of extensions.

[0144]

[Table 4]

| 南條 | _       | 比抵抗值       | <b>厚み分布</b> 比粧抗値 ボトル径<br>(%) (×10 <sup>8</sup> 変化率<br>Ω·cm) (%) | 比抵抗值<br>(×10 <sup>8</sup><br>O·cm) | 比抵抗值<br>(×10 <sup>8</sup><br>Ω·cm)<br>0.32 | 比据抗値<br>(×10 <sup>8</sup><br>Ω·cm)<br>0.32<br>0.27 | 比抵抗値<br>(×10 <sup>8</sup><br>Ω·cm)<br>0.32<br>0.27<br>0.31 | 比抵抗値<br>(×10 <sup>8</sup><br>Ω·cm)<br>0.32<br>0.37<br>0.37<br>0.31<br>0.32 | 上抵抗値<br>(×10 <sup>8</sup> Ω·cm)<br>0.32<br>0.37<br>0.31<br>0.65 | 出機等語<br>(×10 <sup>8</sup><br>32 0.032<br>0.32<br>0.31<br>0.32<br>0.03<br>0.05<br>0.05<br>0.03<br>0.05<br>0.05<br>0.05<br>0.05 |   | 比海流<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10°<br>(×10° |   |
|----|---------|------------|---|------------------------------------|--|--|--|--|---|---|---|---|---|
|    | 収縮 厚み分割 | -          |   |                                    |  |  |  |  | <del></del>   |   | <del></del>   | <del></del>   | <del></del>   |
| -  | -       | (MPa)      | -   | 12                                 | 12 12                                      | 21 21 41   | 8  | 12 12 14 14 10 10  | 8 0 1 1 4 1 4 1 4 1   | 21 14 8 01 41 11  | 8 8 1 12 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1                    | 8 8 8 1 1 1 1 1 1 1 1 2 1 2 1 2 1 2 1 2   | 21 21 4 8 8 8 1 1 2 2 1 2 2 1 2 2 2 2 2 2 2 2 2   |
|    | SRz     | (m m)      |   | 0.74                               | 0.75                                       | 0.74   | 0. 75  | 0. 74<br>0. 75<br>0. 74<br>0. 79<br>0. 77                                  | 0. 75<br>0. 75<br>0. 79<br>0. 79<br>0. 77<br>0. 75              | 0. 74<br>0. 75<br>0. 74<br>0. 79<br>0. 77<br>0. 75  | 0. 74<br>0. 75<br>0. 74<br>0. 77<br>0. 75<br>0. 75<br>0. 75 | 0. 74<br>0. 75<br>0. 74<br>0. 79<br>0. 77<br>0. 75<br>0. 78<br>0. 78  | 0. 74<br>0. 75<br>0. 74<br>0. 79<br>0. 77<br>0. 75<br>0. 78<br>0. 88                    |
|    | ć       |            |   | 0.012                              | 0.012                                      | 0.012  | 0. 012<br>0. 012<br>0. 011                                 | 0. 012<br>0. 011<br>0. 014<br>0. 013                                       | 0. 012<br>0. 011<br>0. 011<br>0. 013                            | 0. 012<br>0. 011<br>0. 011<br>0. 013<br>0. 012  | 0.012<br>0.011<br>0.011<br>0.013<br>0.012<br>0.012          | 0.012<br>0.011<br>0.011<br>0.013<br>0.012<br>0.012<br>0.012   | 0.012<br>0.011<br>0.011<br>0.013<br>0.012<br>0.012<br>0.012<br>0.017                    |
|    | 熟収縮率差   | (%)∇       | ç   | )                                  | 1  | ===  | 11 11 12   | 11 11 11 11  | 5   | 1 1 1 1 1 1 1   | 11 12 12 11 10 01   | 8 0 0 1 1 2 2 2 2 2   | 5   |
|    |         | 直交方向       | -   |                                    | <sub>ا</sub>                               | 8 E  | 8 8 3  | 1   3   2   2  | 8 1 2 2 7   | 8 1 2 7 -   | 1 2 1 2 1 1 0   | 1 2 1 1 1 1 2 1 1 1 2 1 1 1 1 1 1 1 1 1   | 1 2 2 1 - 0 - 1   |
| -  | (B)     | 最大収縮<br>方向 | 78  |                                    | 78   | 78   | 78 78 76   | 78<br>78<br>76<br>76   | 78 76 76 76 76  | 78<br>76<br>76<br>76  | 78<br>78<br>76<br>76<br>77<br>73                            | 78<br>76<br>76<br>77<br>77<br>78<br>70  | 78<br>76<br>76<br>77<br>77<br>78<br>70<br>70  |
|    |         | ર્લે       | 50  | 0                                  | 30   | 43   | 30   | 30   | 30 30 13  | 30<br>30<br>15<br>42  | 30 30 13 13 13 13 13 13 13 13 13 13 13 13 13                | 30 30 30 30 30 30 30 30 30 30 30 30 30 3  | 30<br>30<br>15<br>15<br>15<br>15<br>15<br>15<br>15<br>15<br>15<br>15<br>15<br>15<br>15  |
| _  |         |            | .ルムNo. 1  | 2 0NAJ1                            |  | ILANo. 3   | 164No. 3   | 1/4No. 3<br>1/4No. 4<br>1/4No. 5   | 1.4No. 3<br>1.4No. 4<br>1.4No. 5<br>1.4No. 6                    | 1.4.No. 3<br>1.4.No. 4<br>1.4.No. 6<br>1.4.No. 6  | 1/4No. 3<br>1/4No. 5<br>1/4No. 6<br>1/4No. 6<br>1/4No. 7    | 1/400.3<br>1/400.4<br>1/400.5<br>1/400.7<br>1/400.7   | 1.4.6.0.3<br>1.4.6.0.3<br>1.4.6.0.5<br>1.4.6.0.6<br>1.4.6.0.0<br>1.4.6.0.9<br>1.4.6.0.9 |

[0145] [Table 5]

|               | 耐ブロッキング性 | 走行性 | 耐破れ性 |
|---------------|----------|-----|------|
| 711/4No. 1    | 0        | 4   | 22   |
| 74164No. 2    | 0        | 4   | co.  |
| 71/LANO. 3    | 0        | 4   | S    |
| 74/LLNO. 4    | 0        | 4   | Ф    |
| 741LLNO. 5    | 0        | 4   | ю    |
| 74/LANO. 6    | 0        | 4   | 2    |
| 74.1LGNO. 7   | 0        | 4   | ß    |
| 71/L4No. 8    | 0        | 4   | 2    |
| 71/L4No. 9    | 0        | 4   | ß    |
| 74JL LANO. 10 | ×        | -   | 19   |
| 74164No 11    | c        | L   | 7    |